

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

Publication number:

0 678 597 A1

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: **94302859.7**

(51)

Int. Cl.⁶: **C25D 13/02, C25D 13/16**

(22)

Date of filing: **21.04.94**

(43)

Date of publication of application:
25.10.95 Bulletin 95/43

(84)

Designated Contracting States:
DE FR GB

(71)

Applicant: **UNITED TECHNOLOGIES CORPORATION**
United Technologies Building
1, Financial Plaza
Hartford, CT 06101 (US)

(72)

Inventor: **Dalzell, William J., Jr.**
18290 Jupiter Landings Drive
Jupiter,
Florida 33458 (US)
Inventor: **Wright, Robert J.**
23 Willow Road
Tequesta,
Florida 33469 (US)
Inventor: **Spence, Jarrett L.**
12319 North 182nd Place
Jupiter,
Florida 33458 (US)

(74)

Representative: **Tomlinson, Kerry John**
Frank B. Dehn & Co.
European Patent Attorneys
Imperial House
15-19 Kingsway
London WC2B 6UZ (GB)

(54)

Electrophoresis process for preparation of ceramic fibers.

(57)

A method is taught for the preparation of ceramic fibers by electrophoretic deposition of metal oxide upon a conductive fiber core, which core may be subsequently removed.

EP 0 678 597 A1

Technical Field

The present invention relates to the general area of ceramic materials, and particularly the application of a thick oxide or mixed oxide coating to a filament, wire, or tow by electrophoretic deposition of a colloidal material from a sol to form a ceramic fiber. More particularly, it relates to the use of sols of ceramic materials, such as the oxides of aluminum, yttrium, and mixtures thereof, such as Ytria-Alumina-Garnet, or YAG, and their deposition on substrates by electrophoresis, to provide even, dense, and uniform fibers, while avoiding the costly preparatory steps of prior art techniques for ceramic deposition on a substrate.

Background Art

It is well known to apply coatings to the surface of a body so as to obtain surface properties which differ from those of the body. This may be done to achieve a variety of improvements, such as increased toughness, high temperature capability, oxidation resistance, wear resistance, and corrosion resistance. By providing surface coatings of the appropriate characteristics, it is possible to substantially lower the cost of an article built to specific property requirements. For example, ceramics have frequently been utilized to provide a surface coating over a less temperature resistant metallic article to permit use of that article in higher temperature environments. In addition, ceramic materials are frequently utilized to provide enhanced strength in metal matrix composites by inclusion in the form of powders, fibers, and whiskers. There is a need for ceramic fibers for use in metal matrix composites, particularly those fibers comprising oxides, mixed oxides, or doped oxides, which fibers act as reinforcing elements.

In the past, various processes have been used to deposit ceramic materials upon a substrate. These include the application of glazes, enamels, and coatings; hot-pressing materials at elevated pressure and temperature; and vapor deposition processes such as evaporation, cathodic sputtering, chemical vapor deposition, flame spraying, and plasma spraying. In addition, electrophoresis has been attempted, as have other specialized techniques, with limited success in application.

For example, the enamelling industry has used the electrodeposition of ceramic materials for some time. In the application of a ceramic coating by this technique, a ceramic material is milled or ground to a small particulate or powder size, placed into suspension, and electrophoretically deposited on the substrate. Another traditional method is the deposition of a ceramic coating from a slurry made up of a powder in suspension, usually in an aqueous medium. A major problem with these techniques is that powder particle sizes below about 2 microns were difficult to obtain, thus limiting the quality of coatings produced, as well as the possibility of application to a wire or fibrous substrate.

Sol-gel technology has recently evolved as a source of very fine sub-micron ceramic particles of great uniformity. Such sol-gel technology comprises essentially the preparation of ceramics by low temperature hydrolysis and peptization of metal oxide precursors in solution, rather than by the sintering of compressed powders at high temperatures.

In the prior art, much attention has been given to the preparation of sols of metal oxides (actually metal hydroxide or metal hydrate) by hydrolysis and peptization of the corresponding metal alkoxide, such as aluminum sec-butoxide $[\text{Al}(\text{OC}_4\text{H}_9)_3]$, in water, with an acid peptizer such as hydrochloric acid, acetic acid, nitric acid, and the like. The hydrolysis of aluminum alkoxides is discussed in an article entitled "Alumina Sol Preparation from Alkoxides" by Yoldas, in American Ceramic Society Bulletin Vol. 54, No. 3 (1975), pages 289-290. This article teaches the hydrolysis of aluminum alkoxide precursor with a mole ratio of water:precursor of 100:1, followed by peptization at 90° with 0.07 moles of acid per mole of precursor. After gelling and drying, the dried gel is calcined to form alumina powder.

In U.S. Patent 4,532,072, of Segal, an alumina sol is prepared by mixing cold water and aluminum alkoxide in stoichiometric ratio, allowing them to react to form a peptizable aluminum hydrate, and peptizing the hydrate with a peptizing agent in an aqueous medium to produce a sol of an aluminum compound.

In Clark et al, U.S. Patent 4,801,399, a method for obtaining a metal oxide sol is taught whereby a metal alkoxide is hydrolysed in the presence of an excess of aqueous medium, and peptized in the presence of a metal salt, such as a nitrate, so as to obtain a particle size in the sol between 0.0001 micron and 10 microns.

In Clark et al, U.S. Patent 4,921,731, a method is taught for ceramic coating a substrate, such as a wire, by thermophoresis of sols of the type prepared by the method of U.S. Patent 4,801,399.

It is thus seen that a need exists for a method for the electrophoretic deposition of thick ceramic coatings on a filament, fiber tow, or wire substrate so as to form a ceramic fiber. There is a particular need for a method for the preparation of ceramic fibers for use as reinforcing elements in metal matrix composites.

SUMMARY OF THE INVENTION

In the pursuit of a method for the preparation of defect-free ceramic fibers, applicants have developed a novel electrophoretic deposition process especially suitable for the preparation of metal oxide fibers.

5 As used herein, the term "filament" shall refer to a single strand of fibrous material, "fiber tow" shall refer to a multi-filament yarn or array of filaments, a "wire" shall refer in general to metallic filaments or tows, a "fiber core" shall indicate a filament, fiber tow, or wire suitable for coating by the process of this invention, and the term "ceramic coated fiber" or "coated fiber" shall refer to a fiber core of an electrically conductive material, or a material which has been made to be conductive such as by a flash coat of carbon
10 or a metallizing layer, upon which has been deposited a uniform ceramic layer, such that the diameter of the fiber core is greater than the thickness of the applied ceramic. Conversely, for convenience, the term "ceramic fiber" or "fiber" shall refer to an electrically conductive fiber core material upon which has been deposited a uniform ceramic layer, such that the thickness of the ceramic layer exceeds the diameter of the fiber core. This distinction of relative thickness of surface layer and core is normally recognized in industry
15 to define between coated fiber and fiber. In either case, of course, the fiber core material may be removed by such techniques as acid dissolution, combustion, etc., to leave a hollow ceramic cylinder, which may, of course, then be referred to as a ceramic fiber.

It is an object of this invention to provide a method for the electrophoresis of a sol so as to provide a ceramic fiber. It is a still further object of this invention to provide a method which may be utilized to obtain
20 a highly uniform, defect-free ceramic fiber.

The present invention provides a method for the preparation of a ceramic fiber, said method comprising the steps of:

- a) providing a sol comprising metal hydrate particles selected from the group consisting of aluminum hydrate, yttrium hydrate, and mixtures thereof, said particles being less than 150 Angstroms in size, said
25 sol also comprising an alcohol such that the molar ratio of said alcohol to said metal hydrate is from about 50 to about 70;
- b) electrophoretically depositing particles from said sol onto an electrically conductive fiber core by applying a direct current potential between said fiber core and an anode, said potential being from about 0.1 to about 100 volts, for sufficient time to obtain a uniform deposit of metal hydrate on said fiber core,
30 said deposit being thicker than the diameter of said fiber core, while providing means for removal of hydrogen gas generated by said electrophoresis;
- c) removing the metal hydrate coated fiber core from said sol;
- d) heating the metal hydrate coated fiber core to dry the coating and to transform said metal hydrate to the corresponding metal oxide; and
35 e) recovering the ceramic fiber.

The present invention further provides a method for the continuous production of a metal oxide fiber, comprising:

- a) continuously passing an electrically conductive fiber core through an electrophoresis cell containing a sol prepared by the steps of
40 (1) concurrent hydrolysis and alcoholization of an organometallic compound in an aqueous medium comprising water and an alcohol;
- (2) peptization of this reaction mixture with a monovalent acid or acid source;
- (3) dehydration and de-alcoholization of the reaction mixture by removal of the excess aqueous phase;
- 45 (4) dewatering and further removal of unreacted alcohol by evaporation; and
- (5) re-alcoholization by addition of a second alcohol to the concentrated sol to form a sol wherein the molar ratio of alcohol to metal hydrate is from about 50 to about 70, and the particle size of said metal hydrate is from about 10 to about 150 Angstroms;
- b) applying a potential between said fiber core and another electrode immersed in said sol, whereby
50 metal hydrate particles are continuously deposited on said fiber core to a thickness greater than the diameter of said fiber core;
- c) decreasing the evolution of hydrogen by operating said electrophoresis cell at a potential of from about 1 to about 50 volts;
- d) providing means for the dispersal and removal of hydrogen gas from the electrophoresis cell; and
55 e) heating the fiber core and metal hydrate particles deposited thereupon after said fiber core emerges from said sol, so as to form a metal oxide fiber.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents a schematic of apparatus suitable for use in the present invention for the application of ceramic coatings to a fiber core from a sol by electrophoresis.

5

DETAILED DESCRIPTION OF THE INVENTION

The present invention is suitable for use in producing ceramic fibers. In addition, the sol disclosed herein may be used to produce multi-layer coatings of ceramic on fiber, or to obtain composite coatings by the incorporation of filler materials therein prior to electrophoresis.

10

The sols utilized in the method of the present invention may be produced from a variety of organometallic compounds, to yield metal oxides such as alumina, chrome-ion doped alumina, yttria, and mixtures thereof, such as Yttria-Alumina-Garnet, $3Y_2O_3 \cdot 5Al_2O_3$. While the present disclosure is specifically directed to the use of alumina, chrome-ion doped alumina, and yttria sols, the invention is not to be limited thereto, and should be considered to be applicable to sols of the prior art, subject to the determination of specific modifications necessary.

15

Electrophoresis is an electrodeposition technique whereby minute particles of a normally nonconductive material in colloidal suspension are subjected to an external electric field and thereby caused to migrate toward a specific electrode. Colloids in solution are known to develop a surface charge relative to the suspension medium, as a result of any of a number of possible mechanisms, such as lattice imperfection, ionization, ion absorption, and ion dissolution. In the case of metal oxides such as alumina, the surface charge is the result of ionization, and is generally positive in the preferred pH range, below about 7.

20

During electrophoresis, the positively charged colloids migrate toward the cathode, forming a compact layer of particles thereupon. The physical properties of the deposited coatings are related to their compaction on, and adherence to, the substrate. Generally, the greater the compaction of the colloidal particles deposited upon the substrate, the better the mechanical properties of the coating and the greater the protection afforded thereby.

25

The present invention may be utilized to electrophoretically deposit coatings on a wide range of substrates, both metallic and non-metallic. Exemplary fiber core materials include carbon, glass, silicon carbide, silicon nitride, and metals such as aluminum, iron, nickel, tantalum, titanium, molybdenum, tungsten, rhenium, niobium, and alloys thereof. In general, any material known to be electrically conductive, or which may be made electrically conductive, is capable of being utilized. The diameter of the fiber core is not critical, and may be chosen in accordance with the desired diameter and end usage of the fiber to be produced. Core diameters of from about 0.1 mil (2.5 micrometres) to about 3 mil (76 micrometres) are suitable, recognizing the goal of achieving a ceramic layer which is thicker than the fiber core, and the possible elimination of said core. The final diameter of the fiber produced may be from about 0.3 mil (7.6 micrometres) (or smaller) to about 10 mil (250 micrometres) (or larger) depending upon the strength and other characteristics required.

30

In accordance with the present invention, organometallic compounds are hydrolyzed and peptized to obtain a sol having a colloidal particle size of from about 10 Angstroms to about 150 Angstroms. A preferred range of particle size is from about 50 Angstroms to about 100 Angstroms. Within these ranges of particle sizes, good contact of the coating materials is attained with the fiber core, giving excellent adhesion, and excellent packing of the coating particles within the coating layer is obtained, resulting in superior coating properties such as wear resistance, and thermal high temperature capability.

35

Sols suitable for use in the present invention may be prepared by the hydrolysis and peptization of the corresponding organometallic compounds in an aqueous medium. Preferred organometallic compounds are metal alkoxides, and particularly the metal sec-butoxides, ethoxides, and methoxides of aluminum, yttrium, and mixtures thereof.

40

The process of the present invention comprises a method for the electrophoresis of sols preferably designed for that express purpose. To achieve success, it is desirable to utilize a colloid sol having very small particle size, e.g. less than about 150 Angstroms in diameter. We have found that this may be achieved by the use of a sol which differs from those of the prior art in that in its preparation, hydrolysis of the metallic precursor occurs in the presence of a molar excess of organic solvent, a dehydration/de-alcoholization step occurs after peptization, and after concentration of the sol by removal of water by such means as evaporation, an alcohol transfer reintroduces alcohol in a molar ratio of up to 70 moles of alcohol per mole of metal hydrate present. While the phase transformation reactions occurring during the specific order of the steps of this process are not fully understood, it is theorized that cross-linkage of the AIOOH species during the dewatering and de-alcoholization steps results in a final deposition after electrophoresis

50

55

in accordance with the present invention which is less prone to cracking, spallation, peeling, or flaking. The re-addition of alcohol after concentration of the sol, i.e. re-alcoholization, results in the production of extremely small colloid particles, and an extremely stable sol having a long shelf life and favorable characteristics for electrophoresis. It is to be noted that individual sols may be tailored by choice of organic solvent, peptizer, and additive alcohol utilized.

In general, the process for preparation of the preferred sols for electrophoresis is comprised of the following steps:

a) concurrent hydrolysis and alcoholization of an organometallic compound in an aqueous medium comprising water and an organic solvent;

b) peptization of this reaction mixture with a monovalent acid or acid source;

c) dehydration and de-alcoholization of the reaction mixture by removal of the excess aqueous phase, e.g. by decanting or pipetting;

d) dewatering and further removal of unreacted alcohol by evaporation, also referred to as concentration and/or volume reduction, generally by a vigorous boiling; and

e) re-alcoholization or introduction of additional alcohol to the concentrated sol to form a sol suitable for electrophoresis.

The above procedure is subject to very close control of the proportions of materials utilized, and their molar ratios at the various stages of the procedure. Table I sets forth broad, preferred, and most preferred ranges of the molar ratios of materials during the steps of this procedure, as well as the extent of dewatering/de-alcoholization and volume reduction of the sol.

TABLE I
Parameters for Preparation of Preferred Sol

Parameter	Broad	Preferred	Most Preferred
Molar ratio, organometallic compound to water	0.005 - 0.03	0.006 - 0.02	0.008 - 0.15
Molar ratio, organic solvent to organometallic compound	1.0 - 5.0	1.8 - 3.2	2.3 - 2.7
Molar ratio, peptizer to organometallic compound	0.05 - 0.3	0.08 - 0.23	0.125 - 0.175
Percentage of excess aqueous phase removed during dehydration/de-alcoholization	90 - 100	95 - 100	98 - 100
Percentage of volume reduction during dewatering (concentration)	50 - 75	58 - 72	60 - 70
Molar ratio, added alcohol to metal hydrate in concentrated sol	50 - 70	55 - 69	58 - 67

It is to be noted that the present invention is premised upon a number of principals which have not been appreciated in the prior art. First, it has been known in the prior art that the evolution of hydrogen during electrophoretic deposition is a source of many problems and defects in the coatings obtained. In fact, the application of voltages above about 3 volts DC may result in hydrogen evolution. The present invention uses a number of techniques to overcome these problems by preventing, to the extent possible, the evolution of hydrogen gas, and by then providing means for the dispersal and removal of that hydrogen

which does evolve. These goals are achieved by replacement of water in the sol, to the greatest extent possible, with an organic solvent, e.g. an alcohol; by utilizing a low potential in combination with moving the fiber core at an appropriate rate of speed to establish the thick deposition layer desired and permitting hydrogen to escape; providing means to prevent hydrogen bubbles from embedding in the layer of material formed by the electrophoretic deposition; closely controlling sol content and density so as to maintain the minimum concentration of water at the electrodes; and, generally, operating at appropriate voltages and rates of deposition and fiber core throughput to achieve the goal of a hydrogen-free deposition.

A sol suitable for use in the present invention may be prepared in the following manner, with particular attention being given to prevention of exposure of the reaction mixture to air. While the example is specific to the preparation of an alumina forming sol formulated from an aluminum sec-butoxide precursor, the present invention is not to be limited thereto.

Example 1

For the preparation of an alumina sol, a 4000 ml glass reaction vessel was assembled with a variable temperature heating mantel, glass/teflon stirring rod with a laboratory mixer having variable speed control, an injection port with a teflon tube for insertion of liquids to the bottom of the reaction vessel, and a water-cooled pyrex condenser. After turning on the flow of cooling water to the condenser, 2500 grams (corresponding to 138.8 moles or 2500 ml) of deionized water was metered into the closed reaction vessel, after which the heating mantel was turned on to raise the temperature of the water to between 88 °C and 93 °C, which temperature was thereafter maintained. The mixer motor was turned on when the water had reached this temperature, and the water was vigorously stirred. In a separately sealable glass transfer container, 357.5 grams (corresponding to 1.5 moles or 357.5 ml) of aluminum sec-butoxide $[\text{Al}(\text{OC}_4\text{H}_9)_3]$ was mixed with 288.86 grams (corresponding to 3.897 moles or 357.5 ml) of 2-butanol. Experience has taught that exposure of this mixture, or the aluminum sec-butoxide, to air for any longer than the absolute minimum necessary adversely affected the sol produced, so great care was exercised to avoid exposure. The mixture of sec-butoxide and butanol, in the transfer container, was connected to the reaction vessel entry port after the water had reached the desired temperature, and very slowly, over a 5 minute period, metered directly down into the hot deionized water. When all of the mixture had been introduced into the water, the entry port was valved shut and the transfer container removed. The mixture of water, sec-butoxide, and butanol was then permitted to hydrolyse for a period of 1 hour at temperature while stirring vigorously.

After 1 hour, and with the mixture still at temperature and being stirred vigorously, the sol mixture was peptized by connecting a glass syringe containing 8.18 grams (0.224 moles or 6.875 ml) of hydrochloric acid to the vessel entry port. The entry valve was opened and the acid metered directly down into the sol mixture. The valve was then closed, and the syringe removed and refilled with air. The syringe was then reconnected to the entry port, and the air injected into the vessel to ensure that all of the acid had been introduced into the system. The valve was then closed, and the syringe removed.

The heat and stirring were maintained until the sol cleared, about 16 hours. The heat was then turned off and the stirrer and motor assembly removed. After the mixture cooled, the sol and alcohol separated, and the alcohol was removed by pipette. It was found that leaving a small amount of alcohol in the sol did not adversely affect the sol. The pH of the sol was measured and found to be pH 3.90. This initial sol was found to have a good shelf life, and could be stored prior to further processing to obtain a sol suitable for electrophoresis.

A sol was then specifically formulated for the express purpose of making coated fibers in a continuous process. This specific formulation was also found to be suitable for coating fiber cores or other substrates with a composite coating material, wherein the composite included any chopped fiber material, platelets, powder, or particulates, of metals or other materials in the alumina matrix.

This sol was derived from the initial sol prepared above. A 390 ml sample of the sol prepared above was heated in an open glass beaker to a temperature of approximately 93 °C, and the volatiles, alcohol and excess water, evaporated off. The sol was heated until it had been reduced to 250 ml, i.e. to 64 percent of its initial volume, with a noted increase in viscosity. The reduced sol was then removed from the heat and permitted to cool to room temperature. The reduced sol was then re-alcoholized with 750 ml of ethyl alcohol (63 moles of alcohol/mole of aluminum hydrate present). The sol and alcohol were vigorously mixed, then sealed in an air tight container for storage. The pH of this sol was about pH 3.8. This sol was set aside for 5 months, demonstrating good shelf life, and then subjected to electrophoretic deposition.

To electrophoretically deposit a thick ceramic oxide coating on a filament, fiber tow, or wire, hereinafter fiber core, apparatus such as shown generally in Figure 1 may be used. Any fiber core may be coated with

a ceramic in accord with this invention, if it is electrically conductive, or can be so treated as to be made electrically conductive. For example, fibers of aluminum, carbon, copper, silver, platinum, etc., are normally conductive, while fibers of cotton, polyester, etc., must be made conductive to be used in the present invention. Such fibers may, for example, be coated with a conductive metal or carbon, by conventional coating techniques such as flame spray, plasma spray, etc.

A fiber core may be electrophoretically coated by applying a controlled electrical potential within a colloidal solution of charged particles, with the colloids being driven towards the fiber, at a specific rate controlled by the sol chemistry and the applied electrical potential between the metallic electrodes. The metal anode may be copper, aluminum, silver, gold, platinum, or another electrically conductive metal, but platinum is the preferred material for the anode. The fiber core, being electrically conductive, is the cathodic surface for purposes of electrophoresis of a positively charged sol. If a basic peptizer is utilized in preparation of the sol, the electrodes would, of course, be reversed. The colloidal particles collect in a uniform manner about and along the fiber core, producing a thick, dense, uniform, adherent coating, the chemistry and mechanical properties of which are determined by the sol chemistry, applied electrical potential, and post-coating heat treatment. As a continuous length of fiber core is drawn through the sol, the coating process is effectively continuously repeated. Depending on the coating structure desired, after the fiber core is coated it may be drawn through a furnace, laser, or other heat source, at an appropriate temperature. The process may be better understood from an examination of Figure 1.

A sol, or colloidal solution, 10, is contained in a sol reservoir 12, having a membrane 14, at the lower end. A conductive fiber core 16, from supply spool 18, is first cleaned (at cleaner 20) by a heat source, such as a laser or furnace, a chemical bath, or other suitable cleaning means, prior to contacting either a pair of or a single roller or pulley 22, which is connected to a variable DC power source 24. The fiber core thence passes through the sealing membrane 14, through the sol 10, and through the annular anode 26. It is noted that while the drawing illustrates a vertical anode/sol reservoir, it is possible to have the reservoir and anode disposed horizontally, or at any appropriate angle. The length of the anode may be readily increased by this positioning, and may be extended to 20 feet or longer. After having been electrophoretically coated during passage through the annular anode 26, the coated fiber core passes through a furnace or furnaces 28, for drying and phase transformation of the coating. The furnaces are illustrated as being electric, with AC power sources 30, but any form of heating source may be utilized. The ceramic coated fiber core may now be collected on take-up spool 32. If the coating material is permitted to deposit to a thickness greater than the fiber core, this may now appropriately be referred to as a ceramic fiber.

Such apparatus is useful for the production of ceramic fibers, dependent upon control of variables such as rate of fiber core passage through the annular anode, applied potential at the anode, density of the sol, and extent of hydrogen bubble removal measures. These factors are determinative of the degree of success achieved in the preparation of defect-free, uniformly distributed, compact, and strongly adherent ceramic fibers. The removal of hydrogen from the deposit is of particular importance, since its presence during the heating and drying steps results in creation of escape paths, and hence cracks.

To decrease hydrogen evolution during electrophoresis, one effective approach is to limit the amount of water present in the sol subjected to electrophoresis, since the disassociation of water to hydrogen and oxygen is the source of bubbles which cause defects in the metal oxide layer deposited. One means to accomplish this is to dewater, or concentrate the sol during preparation thereof, by evaporation of the water present to the greatest extent possible without causing the sol to gel, and then replacing such water in the sol by the addition of an alcohol, such as methanol, ethanol, isopropanol, butanol, etc. It has been found that in sols such as prepared as in Example 1, an alcohol to metal hydrate molar ratio of above 50 is desirable, and that such sols are subject to markedly decreased hydrogen evolution during electrophoresis. Broadly, a molar ratio of alcohol to metal hydrate of from about 50 to about 70 has been found effective, with a preferred range of from about 55 to about 69, and a more preferred range of from about 58 to about 67.

An alternative approach to hydrogen removal is to provide a continuous flow of air bubbles, or bubbles of an inert gas, to sweep the surface of the fiber core and the coating being deposited thereupon. The flow rate of these bubbles, which are preferably large relative to the size of the hydrogen bubbles formed by the electrophoresis, should exceed the rate of movement of the fiber core through the sol, so as to permit the air or inert gas to sweep away any hydrogen formed. The hydrogen is thereby carried to the surface of the sol or top of the electrophoresis cell, where it is released to the atmosphere, or evacuated. Such bubbles may be generated in conventional fashion, or provided from a compressed gas source. This creates an escape path for hydrogen gas at the point of separation of sol and coated fiber.

The rate of fiber core throughput also requires consideration and adjustment of electrical potential to achieve the coating thicknesses desired. Low voltage results in less hydrogen evolution, but also requires a

longer period of electrophoresis to attain a thick deposit. This may be achieved by either slowing the rate of fiber core passage, or lengthening the anode itself. Increased voltage, on the other hand, increases the rate of hydrogen evolution. Accordingly, the rates of fiber core throughput and coating voltage should be adjusted in accordance with the coating thickness desired and the specific sol and fiber core employed. It has been found that potentials of from about 0.1 volt to about 100 volts or higher may be employed, preferably from about 1 to about 50 volts, and most preferably from about 35 to about 50 volts, with the fiber core subjected to a deposition period (i.e. the time of passage of a specified point on the fiber core through the length of the annular anode) dependent upon the specific conductivity of the fiber core, the specific composition of the sol, and the voltage applied. Thus, the coating rate may vary greatly. For example, a fiber core may be coated by a YAG sol at a much faster rate of fiber movement and a much lower voltage than the same fiber may be coated with an alumina sol.

As indicated, variation in the length of the anode will also influence these factors, with a longer anode permitting faster fiber core movement and/or lower voltages to achieve similar results. These parameters may be adjusted as desired. It is noted that for purposes of obtaining defect-free, uniform and strong fibers, it is preferable to operate at throughput rates of from about 1200 to about 1600 feet per hour (about 0.10 to about 0.14 ms⁻¹), and voltages of from 35 to 50 volts, in the presence of a sweeping continuous flow of bubbles, thereby decreasing the formation of cracks or voids in the deposition resulting from the presence of hydrogen. To obtain the best quality fibers, electrophoresis at less than about 50 volts is recommended, although quite acceptable fibers may be obtained at potentials up to 100 volts, in the presence of the flow of bubbles, dependent upon the specific sol and the rate of fiber core passage through the sol.

The removal of hydrogen from the surface of the fiber core may also be aided by mechanical means, such as by vibration, including ultrasonic vibration of the sol.

An additional factor in achieving successful deposition is the density of the metal hydrate in the sol, i.e. the availability of material for deposition. This may be influenced by recirculation of the sol to maintain a nearly constant concentration. A large sol holding tank, not illustrated, may be utilized, with a recirculating pump to cause the flow of sol through the sol reservoir 12, with fresh sol added as appropriate to maintain the desired concentration.

After passage through the sol reservoir, the newly coated fiber core, bearing a deposit of metal hydrate, must be dried. While air drying may be used, this approach is much too slow and limiting for a continuous process and would result in a hydrate coating as opposed to an oxide. Preferably, the coated fiber core should be passed through a heated drying zone, such as a furnace, to remove any water and/or alcohol entrapped by the deposited particulate matter during electrophoresis, and to achieve transformation of the hydrate to the oxide. It is noted that if the thickness of the coating layer is greater than the diameter of the fiber core, a ceramic fiber is obtained, by definition. Dependent upon the time and temperature of this heating or curing step, one may control the degree of phase transformation to obtain the desired phase of alumina, yttria, or alumina-yttria-garnet in the surface layer. The appropriate temperatures for curing of the hydrate are within the skill of the operator and may easily be determined, but temperatures from about 850° F (454° C) to about 1200° F (649° C) and above are appropriate for oxide formation from the metallic hydrate. It is to be noted that in some instances, the fiber core per se is consumed during the curing process, after long periods at elevated temperature, resulting in a "free-standing" ceramic cylinder, tube, or jacket, i.e. ceramic fiber. Depending upon packing density, degree of phase transformation, thickness of ceramic, etc., this ceramic fiber may exhibit varying degrees of flexibility, but in most instances may be wound upon a collection spool of approximately 4 inch diameter or greater. Such flexibility is of great value in the use of such fibers.

Coatings have been applied to various fiber cores in accordance with this invention, to produce ceramic fibers suitable for inclusion in metal matrix composites, wherein the oxide fibers serve as reinforcement and/or strengthening inclusions.

Example 2

An alumina sol produced as in Example 1 was used to electrophoretically deposit a 4 mil (100 micrometres) thick coating on a 0.5 mil (13 micrometres) diameter wire of tungsten - 3 percent rhenium alloy. A strongly adherent coating was obtained by deposition in accordance with the method set forth above, and after curing, a fiber of Al₂O₃ of approximately 8 mil (200 micrometres) cross-section was obtained.

Example 3

A sol comprising alumina doped with 3 weight percent chromium was prepared in accordance with Example 1. Using the deposition process of this invention, a thick layer of chrome ion doped alumina was electrophoretically deposited on a 2 mil (51 micrometres) diameter wire of Incoloy 909 alloy. After curing, an alumina fiber approximately 6 mils (150 micrometres) in diameter was obtained.

Example 4

An alumina sol was subject to electrophoresis at 35 volts as set forth above, utilizing a 12.5 micron wire of tungsten-3 rhenium at a rate of 1500 feet per hour. A coating of 6-8 microns thickness was applied, yielding a fiber having a diameter of about 25-28 microns. When the throughput rate of the fiber core was decreased to 750 feet per hour, at the same potential, the coating thickness doubled, giving an alumina fiber of about 40 microns, illustrating the direct relationship between feed rate and results.

Example 5

A thick coating of alumina hydrate was deposited upon a niobium fiber core by the process above. When cured at 1200 °F (649 °C), the niobium core was oxidized, leaving a hollow cylinder of alumina.

Thus, the present invention demonstrates utility for electrophoretic deposition of ceramic fibers. Such fibers have great potential for use as reinforcement fibers in various matrix composites.

It is to be understood that the above disclosure of the present invention is subject to considerable modification, change, and adaptation by those skilled in the art, and that such modifications, changes, and adaptations are to be considered to be within the scope of the present invention, which is set forth by the appended claims.

Claims

1. A process for the preparation of a ceramic fiber, said process comprising the steps of:

a) providing a sol comprising metal hydrate particles selected from the group consisting of aluminum hydrate, yttrium hydrate, and mixtures thereof, said particles being less than 150 Angstroms in size, said sol also comprising an alcohol such that the molar ratio of said alcohol to said metal hydrate is from about 50 to about 70;

b) electrophoretically depositing particles from said sol onto an electrically conductive fiber core by applying a direct current potential between said fiber core and an anode, said potential being from about 0.1 to about 100 volts, for sufficient time to obtain a uniform deposit of metal hydrate on said fiber core, said deposit being of greater thickness than the diameter of said fiber core, while providing means for removal of hydrogen gas generated by said electrophoresis;

c) removing the metal hydrate coated fiber core from said sol;

d) heating the metal hydrate coated fiber core to dry the coating and to transform said metal hydrate to the corresponding metal oxide; and

e) recovering the ceramic fiber.

2. A process as set forth in Claim 1, wherein said means for removal of hydrogen gas includes means to generate bubbles to sweep hydrogen from the fiber core during electrophoresis.

3. A process as set forth in Claim 1 or Claim 2, wherein said potential is from about 1 to about 50 volts.

4. A process as set forth in Claim 3, wherein said potential is from about 35 to about 50 volts.

5. A process as set forth in any preceding claim, wherein said fiber core is selected from the group consisting of carbon, glass, silicon carbide, silicon nitride, and metals selected from aluminum, iron, nickel, tantalum, titanium, molybdenum, tungsten, rhenium, niobium, and alloys thereof.

6. A process as claimed in Claim 5, wherein said fiber core is selected from carbon, silicon carbide, iron, molybdenum, tungsten, rhenium, niobium, and alloys thereof.

7. A process as claimed in any preceding claim, wherein the ceramic is alumina, and the fiber core is an iron-based alloy.
8. A process as claimed in any preceding claim, further comprising the step of recirculating the sol to maintain the concentration thereof.
9. A process as claimed in any preceding claim, wherein the metal hydrate coated fiber core is heated to a temperature of at least 850 ° F.
10. A process as claimed in any preceding claim, wherein the metal hydrate is aluminum hydrate.
11. A process as claimed in any one of Claims 1 to 9, wherein said metal hydrate is yttrium hydrate.
12. A process as claimed in any one of claims 1 to 9, wherein said metal hydrate is a chrome ion doped aluminum hydrate.
13. A process as claimed in any one of Claims 1 to 9, wherein said metal hydrate is a mixture of aluminum hydrate and yttrium hydrate.
14. A method for the continuous production of a metal oxide fiber, comprising:
 - a) continuously passing an electrically conductive fiber core through an electrophoresis cell containing a sol prepared by the steps of:
 - (1) concurrent hydrolysis and alcoholization of an organometallic compound in an aqueous medium comprising water and an alcohol;
 - (2) peptization of this reaction mixture with a monovalent acid or acid source;
 - (3) dehydration and de-alcoholization of the reaction mixture by removal of the excess aqueous phase;
 - (4) dewatering and further removal of unreacted alcohol by evaporation; and
 - (5) re-alcoholization by introduction of additional alcohol to the concentrated sol to form a sol wherein the molar ratio of alcohol to metal hydrate is from about 50 to about 70, and the particle size of said metal hydrate is from about 10 to about 150 Angstroms;
 - b) applying a potential between said fiber core and another electrode immersed in said sol, whereby metal hydrate particles are continuously deposited on said fiber core to a thickness greater than the diameter of said fiber core;
 - c) decreasing the evolution of hydrogen by operating said electrophoresis cell at a potential of from about 1 to about 50 volts;
 - d) providing means for the dispersal and removal of hydrogen gas from the electrophoresis cell;
 - e) heating the fiber core and metal hydrate particles deposited thereupon after said fiber core emerges from said sol, so as to form a metal oxide fiber.
15. A method as set forth in Claim 14, wherein said fiber core is selected from the group consisting of carbon, glass, silicon carbide, silicon nitride, and metals selected from aluminum, iron, tantalum, titanium, nickel, molybdenum, tungsten, rhenium, niobium, and alloys thereof.
16. A method as set forth in Claim 14 or Claim 15, wherein said metal oxide is selected from the group consisting of alumina, chrome-ion doped alumina, yttria, and yttria-alumina-garnet.
17. A method as claimed in any one of Claims 14 to 16, wherein the thickness of said coating is equal to or greater than the diameter of said fiber core.
18. A method as claimed in any one of Claims 14 to 17, wherein said alcohols are selected from methanol, ethanol, isopropanol, and butanol, and said organometallic compound is selected from the group consisting of the sec-butoxides, ethoxides, and methoxides of aluminum, yttrium, and mixtures thereof.
19. A method as claimed in any one of Claims 14 to 18, wherein said means for dispersal and removal of hydrogen gas comprises means to induce the flow of bubbles of inert gas adjacent the fiber core during its passage through the cell.

- 20.** A method as claimed in any one of claims 14 to 19, wherein the fiber is from about 0.3 mils (7.6 micrometers) to about 9 mils (230 micrometers) in diameter.

5

10

15

20

25

30

35

40

45

50

55

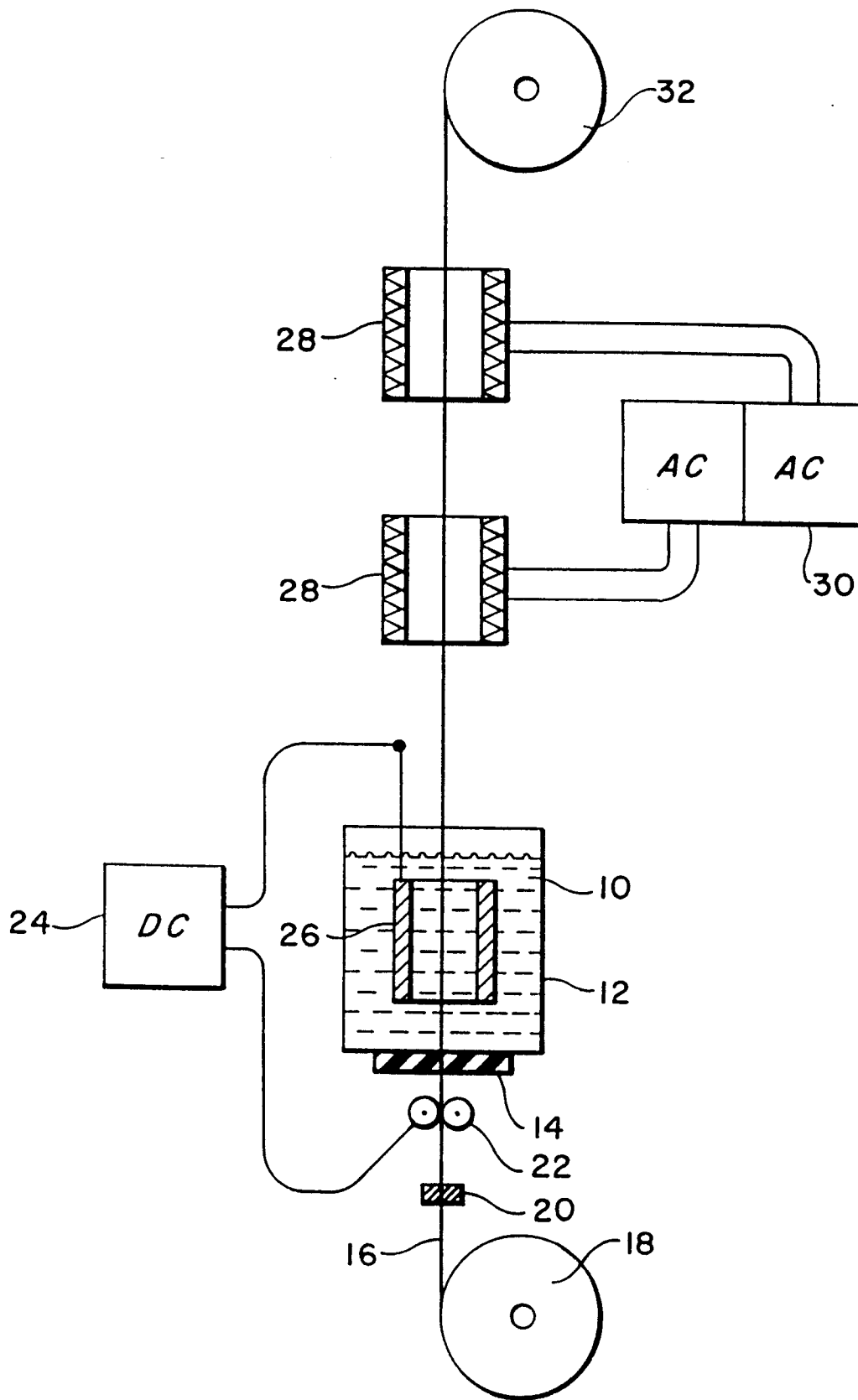


FIG. 1



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 30 2859

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-5 302 319 (WRIGHT) * column 4, line 27 - line 34 * * column 4, line 60 - line 68 * * column 8, line 25 - line 29 * * column 5, line 1 - line 6 * * column 3, line 1 - line 6 * * column 6, line 25 - line 38 * -----	1,5-7, 10-18	C25D13/02 C25D13/16
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C25D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 September 1994	Examiner Nguyen The Nghiep, N
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	